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PATENT SPECIFICATION 586,250



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PROVISIONAL SPECIFICATION

Electrolytic Cleaning of Metals

We, E. I. DU PONT DE NEMOURS AND Co., a corporation organised and existing under the laws of the State of Delaware, United States of America, of Wilmington, Delaware, United States of America, and HARVEY NICHOLAS GILBERT of 1246, Cayuga Drive, Niagara Falls, New York, United States of America, a citizen of the United States of America, do hereby declare the nature of this invention to be as follows:—

This invention relates to the cleaning of metals and more particularly to an electrolytic process employing a fused bath for removing oxide coatings from metal articles.

It is known that metal surfaces may be cleaned by subjecting them to the action of alkali metals or alkaline earth metals in the nascent condition, and that such a condition can be secured by electrolysis in a fused salt or compound of an alkali metal or alkaline earth metal, particularly caustic soda. It is also known that metal surfaces can be cleaned by contacting them with a molten composition comprising one or more alkali metal hydroxides containing dissolved alkali metal hydride. We have now found that excessive corrosion and the formation of excessive amounts of insoluble material in the bath can be avoided by using an electrolytic process employing a fused bath containing alkali metal hydroxide and alkali metal hydride.

According to the present invention we provide a process for cleaning metal articles, particularly for removing oxide coatings from the surface thereof, which comprises electrolysing a solution of

alkali metal hydride in molten alkali metal hydroxide with the said article as cathode. The solution of alkali metal hydride in alkali metal hydroxide may be prepared in any desired manner, e.g. by reacting hydrogen with alkali metal which has been added to, or which is formed in, a fused alkali metal hydroxide bath. The concentration of hydride is generally between 0.5% and 10% by weight, preferably between 1% and 2% by weight.

The preferred temperature range of operation is between 350° and 500° C., but temperatures from 250°—600° C. may be employed.

We prefer to confine the hydride to the vicinity of the cathode in order to avoid loss of hydride by anodic oxidation as much as possible. Baffles or diaphragms may be used in an electrolytic cell for this purpose.

The presence of small amounts of water in the bath, which occurs due to the electrolysis and which may have a harmful effect on the freshly cleaned metal surface, is generally avoided by the addition of sodium monoxide which rapidly reacts with the water and thus keeps the bath fully dehydrated.

The process is of particular importance for descaling iron and steel articles and is also applicable to the removal of surface oxides from nickel, silver, copper and other non-ferrous metals which are not damaged by the hydroxide baths.

Dated the 11th day of December, 1944.

J. W. RIDSDALE,
Solicitor for the Applicants.

COMPLETE SPECIFICATION

Electrolytic Cleaning of Metals

We, E. I. DU PONT DE NEMOURS AND Co., a corporation organised and existing under the laws of the State of Delaware, United States of America, of Wilmington, Delaware, United States of America, and HARVEY NICHOLAS GILBERT of 1246,

[Price 1/-]

Cayuga Drive, Niagara Falls, New York, United States of America, a citizen of the United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and

ascertained in and by the following statement:—

This invention relates to the cleaning of metals and more particularly to an electrolytic process employing a fused bath for removing oxide coatings from metal articles.

It is known that metal surfaces may be cleaned by subjecting them to the action of alkali metals or alkaline earth metals in the nascent condition, and that such a condition can be secured by electrolysis in a fused salt or compound of an alkali metal or alkaline earth metal, particularly caustic soda. Such a process is described and claimed in Specification 442,859. It is also known that metal surfaces can be cleaned by contacting them with a molten composition comprising one or more alkali metal hydroxides containing dissolved alkali metal hydride, as described in Specification 557,530. In such processes utilising molten caustic baths difficulties are often encountered due to excessive corrosion of metal parts in contact with the bath. Generally such corrosion in excess is especially troublesome in regard to deterioration of the container, which usually is a steel tank. Also in some cases difficulty has been encountered with the formation of excessive amounts of insoluble material in the bath, which tends to settle out and form a sludge on the bottom of the container which appears with bottom firing methods of heating the container.

We have now found that excessive corrosion, both of containers for the bath and of metals treated in the bath, and the formation of excessive amounts of insoluble material in the bath, can be avoided by using an electrolytic process employing a fused bath containing alkali metal hydroxide and alkali metal hydride. The present process is also of especial benefit in cases where complete cleaning by electrolytic action in an alkali metal hydroxide bath alone is difficult.

According to the present invention, we provide a process for cleaning metal articles, particularly for removing oxide coatings from the surface thereof, which comprises electrolysing a solution of alkali metal hydride in molten alkali metal hydroxide with the said article as cathode.

The solution of alkali metal hydride in alkali metal hydroxide may be prepared in any desired manner, e.g. by reacting hydrogen with alkali metal which has been added to, or which is formed in, a fused alkali metal hydroxide bath. The concentration of hydride in the bath in the vicinity of the articles being treated should not be less than 0.5% by weight,

and concentrations up to 5% or even 10% by weight may be used, but we prefer to use between 1% and 2% by weight. Methods of preparing suitable baths containing caustic soda and sodium hydride, or other alkali metal hydroxides and hydrides, are described in Specification 557,530. In a preferred method, we make the alkali metal hydride *in situ*, using the fact that the electrolysis of fused alkali metal hydroxide causes the liberation of alkali metal at the cathode, and we introduce hydrogen into the bath, especially in the vicinity of the cathode, so that it may react with the liberated metal to form the hydride. In such cases we prefer to operate the bath at a sufficient cathodic current density so that the amount of alkali metal liberated is in excess of that required to react with the oxide coating which may be on the cathode and with any moisture which may be present in the bath. The amount of hydrogen introduced is preferably molecularly equivalent to at least a major proportion of the liberated metal. Other methods include floating a layer of metallic sodium on the surface of the electrolytic bath, preferably restricted to an area near the work which is undergoing treatment, and bubbling hydrogen under the surface of the sodium so as to form sodium hydride which dissolves in the bath. The hydride may also be formed by reacting hydrogen with sodium floating on a bath of fused alkali metal hydroxide in a separate container, and the solution of hydride thus formed is flowed into the metal cleaning container, preferably near the work undergoing cathodic treatment. Sodium compounds are preferred, but one or more other alkali metal hydroxides and hydrides may also be used.

The preferred temperature range of operation is between 350° and 500° C., but temperatures from 250°—600° C. may be employed. The melting point of the bath must be below the temperature of operation and this generally restricts the lower temperature of operation to 250°—300° C., and the upper limit of the operating temperature should not exceed 600° C. in order to avoid undue decomposition of the hydride.

We prefer to confine the hydride to the vicinity of the cathode in order to avoid loss of hydride by anodic oxidation as much as possible. Baffles or diaphragms adapted to deflect the anodically formed oxygen out of the apparatus without contact with the dissolved hydride and/or the cathode may be used in the electrolytic cell for this purpose.

The presence of small amounts of water

in the bath, which occurs due to the electrolysis and which may have a harmful effect on the freshly cleaned metal surface, is generally avoided by the addition of sodium monoxide which rapidly reacts with the water and thus keeps the bath fully dehydrated.

In a preferred arrangement for carrying out our invention as shown in the accompanying diagram, we place a suitable diaphragm A, for example a sheet of steel, wire gauze or other foraminous steel sheet, between the anode and cathode. We then place one or more baffles B a short distance from the anode, between the anode and the adjacent side wall of the electrolyte container, arranged so that the baffle and the diaphragm cooperate with the gas-lift effect of the oxygen rising from the anode to cause bath circulation. The baffle terminates below the surface of the bath or has one or more openings at that point, so that the electrolyte rising along the anode, after passing over the top of the baffle or through such openings, descends along the side wall. We then introduce sodium monoxide into the bath in the anode compartment, preferably into the descending stream of the circulating electrolyte. The best results are secured by continuously flowing in finely divided, solid sodium monoxide at a rate substantially equal to that required to react with the water formed by the electrolysis. At the same time, we continuously flow hydrogen into the bath in the cathode compartment by the tube C, i.e. on the cathode side of the diaphragm. Preferably, the hydrogen is led in through one or more pipes at a point or points below the cathode or cathodes in the cell, so that the hydrogen bubbles tend to rise around the cathodic surfaces.

In this mode of operation, any excess monoxide in solution will react with the hydrogen in the cathode compartment to form hydride. The hydrogen also reacts

with sodium liberated at the cathode. The monoxide addition maintains the caustic substantially anhydrous at all times. This dehydration approximately doubles the electrical efficiency, as it avoids any substantial loss of sodium metal by reaction with water.

The process is of particular importance for descaling iron and steel articles and is also applicable to the removal of surface oxides from nickel, silver, copper and other non-ferrous metals which are not damaged by the hydroxide baths.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. Process for removing oxide from the surface of a metal article which comprises electrolysing a solution of alkali metal hydride in molten alkali metal hydroxide with said article as cathode.

2. Process as claimed in Claim 1 in which the solution contains sodium hydroxide and sodium hydride, preferably between 1 and 2% by weight of sodium hydride.

3. Process as claimed in either of Claims 1 and 2 carried out at a temperature between 350° and 500° C.

4. Process as claimed in any of the preceding claims in which the hydride is confined to the vicinity of the cathode.

5. Process as claimed in any of the preceding claims in which hydrogen is passed into the bath in the vicinity of the cathode, the amount of hydrogen preferably being molecularly equivalent to at least a major proportion of the alkali metal liberated by cathodic action.

6. Process for cleaning metal articles substantially as hereinbefore described.

7. Metal articles whenever cleaned by the process of any of the preceding claims.

Dated the 7th day of December, 1945.

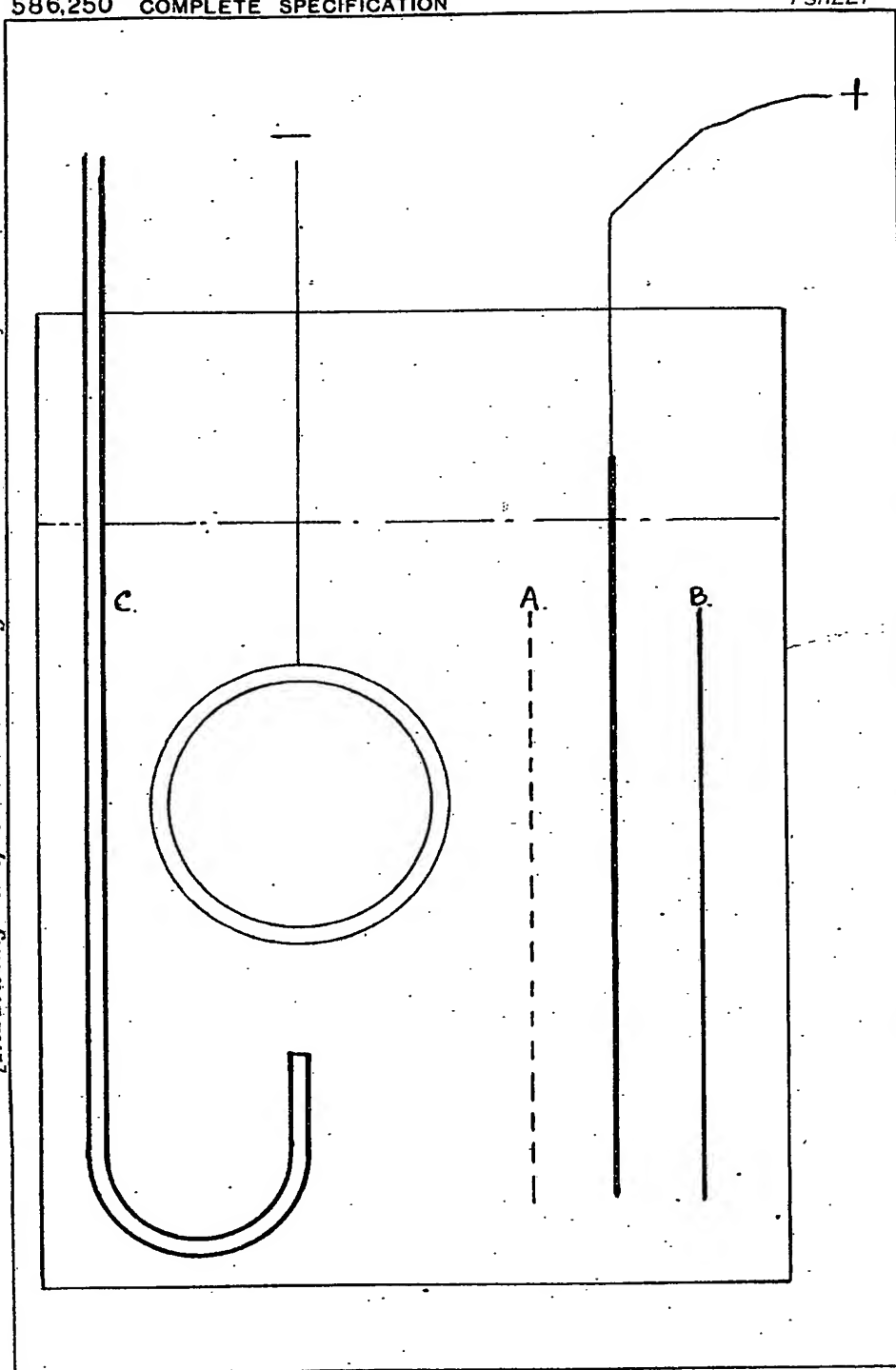
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Solicitor for the Applicants.

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H.M.S.O. (Ty.P.)